

Combined Pb–Sr isotopic analysis in provenancing late Roman iron raw materials in the territory of Sagalassos (SW Turkey)

Patrick Degryse · Jens C. Schneider · Philippe Muchez

Received: 24 March 2009 / Accepted: 10 June 2009 / Published online: 17 July 2009
© Springer-Verlag 2009

Abstract In early Roman times, iron was likely supplied to the city of Sagalassos through the smelting of close-by hematite ores. In the early Byzantine period, magnetite–titanite placer sands in some instances could have been exploited for its iron. For the intermediate late Roman period, however, the source of the locally used iron was unknown. Pb and Sr isotopic analyses of iron ores from the area of Camoluk, just south of the territory of Sagalassos, and of late Roman iron artefacts from the antique city itself, reveal a very close resemblance. This makes the use of the Camoluk ores to supply Sagalassos with raw iron in the late Roman period likely. It is also shown that combined Pb and Sr isotopic analyses provides a powerful tool to distinguish chronological groups of iron provenance and a technique that can determine the nature and source of iron raw materials used.

Keywords Roman period · Sr and Pb isotopic studies · Iron provenance · Turkey

Introduction

In the study of ancient iron production and processing, it is difficult to determine the origin of the raw materials used

(Heimann et al. 2001). In the direct reduction method for preparing raw iron from its ores, the ore is reduced to a bloom or ‘spongy’ iron at 1,150–1,200°C (Wertime 1980) from which the slag drains away as a melt (White 1986). During such process, gangue minerals, furnace fragments and fuel ashes are enriched in the slag, while the iron remains as a metal in the furnace. Due to extensive effects of chemical fractionation that occur during such process, it is difficult to correlate slag material, bloom, iron objects and potential ores solely on the basis of their main and trace element chemistry or mineralogy when ore, slag and bloom of one furnace charge are not found in the same archaeological context (e.g. Buchwald and Wivel 1998; Heimann et al. 2001). However, recent studies have used the chemical–mineralogical analysis of slag inclusions in iron objects as a means of studying ore provenance next to the technological context of production such as furnace types, construction materials, fuel, etc. (e.g. Ferrer Eres et al. 2008). The intention of the use of the radiogenic isotope technique presented here is to falsify a direct relation between a raw material and a finished product, as radiogenic isotope analyses offer a solution to the problem of chemical fractionation (Gale et al. 1990; Schwab et al. 2003; Degryse et al. 2007).

The occurrence of iron smelting and smithing slag in all excavation layers dating from the first to the seventh century AD at Sagalassos (Fig. 1, SW Turkey) proves the processing of iron there (Kellens et al. 2003). In an earlier study, lead and strontium isotope analyses were performed by thermal ionisation mass spectrometry on early Roman to early Byzantine iron artefacts and iron ores from the territory of the town. The use of Pb and Sr isotopes for provenance determination of the ores used for local iron production was thus evaluated (Degryse et al. 2007). It was demonstrated that the ore source for early Roman artefacts from Sagalassos

P. Degryse (✉) · J. C. Schneider · P. Muchez
Geology Section,
Department of Earth and Environmental Sciences,
Celestijnenlaan 200E, bus 2408,
3001 Leuven, Belgium
e-mail: patrick.degryse@ees.kuleuven.be

J. C. Schneider
e-mail: jens.schneider@ees.kuleuven.be

P. Muchez
e-mail: philippe.muchez@ees.kuleuven.be

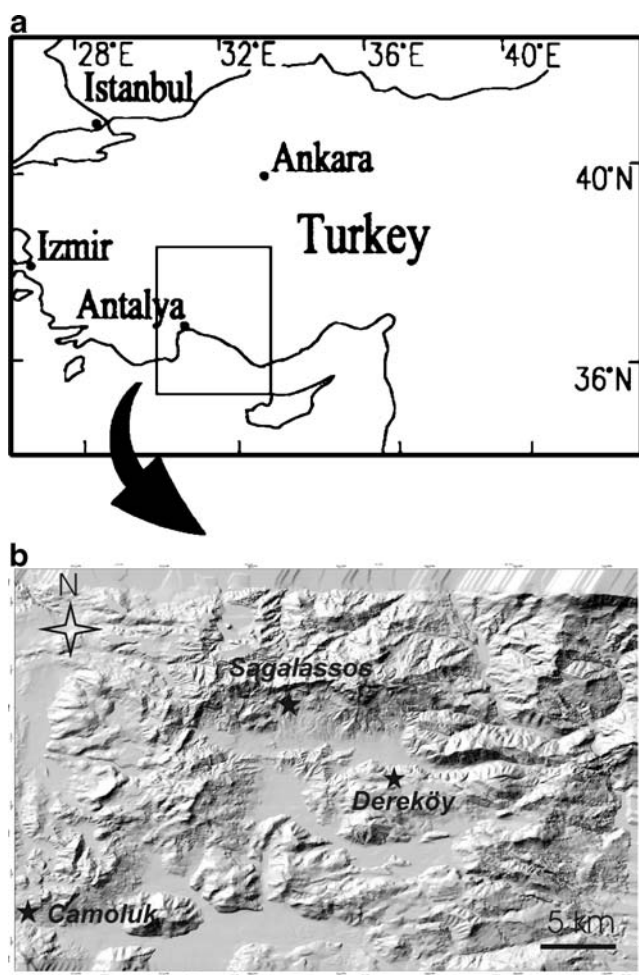


Fig. 1 Map of the territory of Sagalassos with the ancient town, the placer sands at Dereköy and the iron ores of Camoluk indicated

was hematite iron ore from an ore deposit in the Lycean limestone nappes, just north of the ancient town, and that magnetite placer sands were used for early Byzantine raw iron production in the territory of the city at Dereköy (Fig. 1). Sr isotopes proved much less ambiguous than Pb isotopes in providing clearly coherent signatures for ore and related iron objects (Degryse et al. 2007). While lead isotopic signatures of artefacts and ores may be ambiguous due to the often highly variable chemistry of the raw materials, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may represent a more straightforward tool to exclude or corroborate specific point sources of ores used for metal production. Early Byzantine iron artefacts from Sagalassos display more scatter in both their Pb and Sr

isotope signatures, indicating that different ore sources were used for their production. It was shown that late Roman iron objects from Sagalassos had an isotopic signature clearly different from artefacts from the early Roman and most of the early Byzantine periods. Moreover, the signature of the late Roman iron was clearly different from both that of the hematite ore and the magnetite–titanite placer sands from Dereköy, and these artefacts were hence produced from iron ores, which remained unidentified. This ore source needs to be situated outside the territory of Sagalassos, as the aforementioned ore sources were the only ones identified in extensive geochemical–geological prospecting (Degryse et al. 2003a, b).

However, just outside the territory of Sagalassos, a new Fe–Mn mineralization was described at Camoluk (Fig. 1), which is being used in modern steel production (Tekere and Kuşçu 2006). As the deposit is situated close to the southern border of the territory of Roman Sagalassos, along good communication and transport ways, these deposits are evaluated as a possible source for the late Roman and early Byzantine iron at Sagalassos. Iron artefacts of that time were analysed again for their Pb and Sr isotopic signatures (duplicating analyses from Degryse et al. 2007) and were compared to Pb–Sr isotopic analysis of suitable iron ores from Camoluk.

Materials

In the area of Camoluk, around Akpınarkale Tepe, Kulube Tepe and Elmaçukuru, iron–manganese deposits are found in the Duterde Middle Triassic to Lias (Jurassic) limestones (Tekere and Kuşçu 2006). Ore lenses and veins have thicknesses ranging from 0.5 to 2 m and cut through the limestone. Main ore minerals are hematite, goethite, pyrolusite, psilomelane and hausmanite with barite, quartz, calcite and dolomite as gangue minerals. Two samples were taken for isotopic analysis. Sample AC7 from Akpınarkale is mainly hematite with minor pyrolusite and barite and sample EC5 from Elmaçukuru is mainly barite with hematite (Table 1 after Tekere and Kuşçu 2006). Two late Roman iron artefacts from Sagalassos were re-analysed for their Pb–Sr isotopic composition. Sample SA00LL5 is an iron nail, sample SA03NK145 an arrow head (Degryse et al. 2007).

Table 1 Chemical and mineralogical data of the Fe ores analysed for Pb–Sr isotopes (after Tekere and Kuşçu 2006)

| Sample | Location | Mineralogy | Fe ₂ O ₃ | MnO | BaO | SiO ₂ | Al ₂ O ₃ | CaO | MgO | LOI | Sum | Tot C | Tot S |
|--------|-------------|---------------------|--------------------------------|-------|-------|------------------|--------------------------------|------|------|------|-------|-------|-------|
| AC-7 | Akpınarkale | Hematite–pyrolusite | 71.88 | 10.71 | 1.40 | 3.22 | 0.54 | 1.17 | 0.20 | 9.30 | 98.42 | 0.18 | 0.01 |
| EC-5 | Elmaçukuru | Barite–hematite | 22.14 | 0.93 | 40.42 | 1.34 | 0.73 | 1.94 | 0.23 | 5.30 | 73.03 | 0.45 | 9.73 |

Materials and methods

For isotope analysis, ore samples were weighed into Teflon screw-top beakers and dissolved in a 3:1 mixture of 22 N HF and 14 N HNO₃ on a hot plate, dried and dissolved in aqua regia. Iron artefacts (sample weights several hundred milligrams) were completely dissolved in aqua regia. All solutions were spiked with a highly enriched ⁸⁴Sr tracer, which allows for determination of Sr isotopic composition and Sr elemental concentration from one mass spectrometry run. Strontium and lead were chemically separated with 3 N HNO₃ using Eichrom Sr resin on 250-μl Teflon columns, following the combined methods of Horwitz et al. (1991a, b), Vajda et al. (1997) and Gale (1996). Sr was stripped from the columns with 5 ml of H₂O. Subsequently, Pb was eluted from the same column with 5 ml of 6 N HCl. The Pb cut was further processed through a 250-μl column containing Eichrom Pre Filter Resin. After evaporation to dryness, the entire procedure was repeated using 50-μl columns to further purify both the Sr and Pb eluates. For mass spectrometry, Sr was loaded with TaCl₅–HF–H₃PO₄ solution (Birck 1986) onto W single filaments and Pb loaded onto single Re filaments using silica gel–H₃PO₄ bedding. All Sr and Pb isotopic measurements were performed on a six-collector Finnigan MAT 261 solid-source mass spectrometer running in static multicollection mode. Sr isotopic ratios were normalised to ⁸⁸Sr/⁸⁶Sr = 0.1194. Repeated static measurements of the NBS 987 standard over the duration of this study yielded an average ⁸⁷Sr/⁸⁶Sr ratio of 0.71025 ± 4 (2σ mean). Sample Pb isotope ratios were corrected for mass fractionation according to Ludwig (1980), using a mean discrimination factor of 0.123 ± 0.029% per amu (2σ), based upon replicate analyses of the NBS SRM 981 Pb standard. The 2σ uncertainties for the corrected ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios are 0.06%, 0.09%, 0.12%, 0.03% and 0.06%, respectively. Individual a priori uncertainties (2σ) are given for isotope ratios and Sr elemental concentrations (Table 2). Iron artefact samples containing less than 10 ppm Pb and Sr were corrected for maximum total procedure blanks of 30 pg for both Pb and Sr (Degryse et al. 2007). For the ore samples, blank values were found to be negligible (<0.5 wt.% of the analysed sample Pb and Sr amounts).

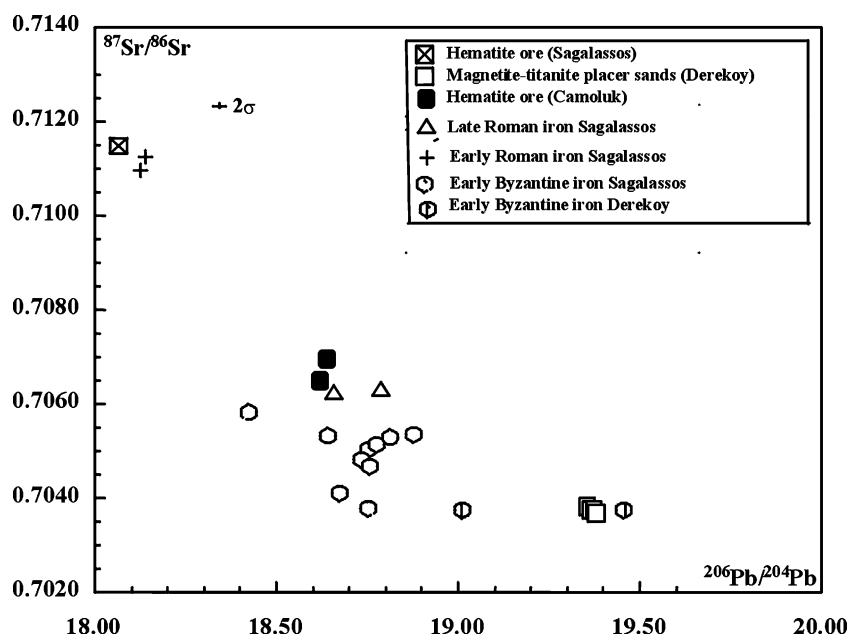
Results

Figure 2 shows ⁸⁷Sr/⁸⁶Sr vs. ²⁰⁶Pb/²⁰⁴Pb diagram for samples of ores and iron artefacts published in Degryse et al. (2007) and two samples of iron ore from Camoluk analysed for this study. The isotope data for the Late Roman iron artefacts and the ores from Camoluk are listed

Table 2 Pb–Sr isotope analysis of iron artefacts and iron ores

| Sample | Location | Nature | ²⁰⁶ Pb/ ²⁰⁴ Pb | 2σ | ²⁰⁷ Pb/ ²⁰⁴ Pb | 2σ | ²⁰⁸ Pb/ ²⁰⁴ Pb | 2σ | ⁸⁷ Sr/ ⁸⁶ Sr | 2σ | Sr (ppm) | 2σ (ppm) |
|------------------|-------------|---------------------|--------------------------------------|-------|--------------------------------------|-------|--------------------------------------|-------|------------------------------------|---------|----------|----------|
| Artefacts | | | | | | | | | | | | |
| SA03NK145 | Sagalassos | Arrow head | 18.777 | 0.012 | 15.667 | 0.015 | 38.846 | 0.049 | 0.70631 | 0.00001 | 8.96 | 0.13 |
| SA03NK145B | Sagalassos | Arrow head | 18.782 | 0.013 | 15.672 | 0.015 | 38.883 | 0.049 | 0.70631 | 0.00001 | – | – |
| SA00LL5 | Sagalassos | Nail | 18.648 | 0.024 | 15.702 | 0.023 | 38.835 | 0.072 | 0.70637 | 0.00001 | 2.27 | 0.03 |
| SA00LL5B | Sagalassos | Nail | 18.650 | 0.025 | 15.698 | 0.020 | 38.824 | 0.068 | 0.70638 | 0.00001 | – | – |
| Iron ore | | | | | | | | | | | | |
| AC-7 | Akpınarkale | Hematite–pyrolusite | 18.618 | 0.015 | 15.701 | 0.015 | 38.62 | 0.059 | 0.70718 | 0.00001 | 682 | 9 |
| EC-5 | Elmacukuru | Barite–hematite | 18.613 | 0.03 | 15.661 | 0.015 | 38.493 | 0.077 | 0.70664 | 0.00001 | 3,237 | 43 |

Fig. 2 $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of the samples analysed in this study and the iron and ores analysed by Degryse et al. (2007)



in Table 2. The early Roman iron artefacts (crosses) and the hematite ore sample from the same context define a cluster at low $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Early Byzantine iron objects from Sagalassos and early Byzantine iron billets from Sagalassos (filled black circles) and from Dereköy (open circles) form a wider cluster but, for most objects, do not correspond to the Camoluk ores, though some objects lie closer to the Camoluk ore isotopic composition than the other ore sources. One iron artefact from Dereköy corresponds to the magnetite placer sands from Dereköy. An excellent correspondence in $^{87}\text{Sr}/^{86}\text{Sr}$ signature can be seen between the ores and both iron billets from Dereköy, whereas lead isotopes are more ambiguous. However, as both ore and iron were found in a single production context, their relation in the smelting activities on the territory is undoubted (Degryse et al. 2007). The late Roman iron from Sagalassos (triangles) has a virtually identical and relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, distinct from most of the early Byzantine artefacts and clearly distinct from the early Roman material. Remarkably, its signature is identical to the ores from Camoluk analysed for this study.

Discussion

A first observation that can be made from the replicate analysis of the late Roman artefacts is the fact that the Sr and Pb isotopic composition of the objects is homogeneous (different samples of the same object were analysed) within analytical error. The Sr isotopic composition of the artefacts in replicate analysis gives identical results.

Secondly, it is clear that there is a good correspondence between the Pb–Sr signature of the late Roman iron

artefacts from Sagalassos and the iron ore samples from Camoluk. This makes these ore deposits a possible candidate for the source of the raw materials used for the iron supply to Sagalassos in the late Roman period, though (many) more analyses are needed to define the exact signature of the late Roman iron artefacts at Sagalassos and the ore field at Camoluk. Although the area of Camoluk was never part of the territory of Sagalassos, it is situated only a few kilometres south of the border of the territory at its maximal extension in Roman times and very close to the Burdur plain, extensively used as an agricultural area for the Roman city. Therefore, trade of iron from Camoluk is not unlikely. In which form such trade would have been set up is unclear, though it is more likely that instead of ore, raw iron was transported. For the late Roman period, unlike the early Roman or early Byzantine period, no traces of iron smelting are known from the territory, while traces of iron smithing in the form of smithing slag can be found in all periods. It may well be that the city in the late Roman period relied entirely on iron brought in from outside its own territory. Furthermore, in the immediate area of the ore sources at Camoluk, no traces of ancient extraction or iron smelting were observed. However, the modern day exploitation is intensive, and the open pit mining would have destroyed superficial traces of ancient working, so that no antique traces are left.

Conclusion

Both iron objects and ores can be precisely analysed for their Sr isotopic composition, which, combined with Pb isotopes, are a powerful tool to distinguish between

chronological groups of iron provenance and can determine the nature and source of raw materials used. Based on the aforementioned isotopic analysis, iron ore deposits situated at Camoluk, close to the territory of Sagalassos, are a possible candidate for supplying raw iron to the territory of the ancient city in late Roman times. The ores are unlikely to have been used in the territory of Sagalassos in early Roman or early Byzantine times.

Acknowledgements This research was supported by the Interuniversity Attraction Poles Programme–Belgian Science Policy (IUAP VI) and presents results of a research project of the Special Research Fund of the K.U. Leuven (GOA 07).

References

- Birck JL (1986) Precision K–Rb–Sr isotopic analysis: application to Rb–Sr chronology. *Chem Geol* 56:73–83
- Buchwald VF, Wivel H (1998) Slag analysis as a method for the characterisation and provenancing of ancient iron objects. *Mater Charact* 40:73–96
- Degryse P, Ph M, Six S, Waelkens M (2003a) Identification of ore extraction and metal working in ancient times: a case study of Sagalassos (SW Turkey). *J Geochem Explor* 77:65–80
- Degryse P, Ph M, Naud J, Waelkens M (2003b) Geochemical prospection for iron-mineralisations (SW Turkey) and their use during Roman–Byzantine times. In: Eliopoulos DG, Allan C, Baker T, Barriga F, Gervilla F et al (eds) *Mineral exploration and sustainable development*. Millpress, Rotterdam, pp 969–972
- Degryse P, Schneider J, Kellens N, Ph M, Haack U, Loots L, Waelkens M (2007) Tracing the resources of iron working at ancient Sagalassos: a combined lead and strontium isotope study on iron artefacts and ores. *Archaeometry* 49:75–86
- Ferrer Eres MA, Valle-Algarra FM, Gimeno Adelantado JV, Peris-Vicente J, Soriano Piñol MD, Mateo-Castro R (2008) Archaeometric study on polymetallic remains from the archaeological dig in Lixus (Larache, Morocco) by scanning electron microscopy and metallographic techniques. *Microchim Acta* 162:341–349
- Gale NH (1996) A new method for extracting and purifying lead from difficult matrices for isotopic analysis. *Anal Chim Acta* 332:15–21
- Gale NH, Bachmann HG, Rothenberg B, Stos-Gale ZA, Tylecote RF (1990) The adventitious production of iron in the smelting of copper. In: Rothenberg B, Bachmann HG (eds) *Researches in the Arabah 1959–1985*. University College, London
- Heimann RB, Kreher U, Spazier I, Wetzel G (2001) Mineralogical and chemical investigations of bloomery slags from prehistoric (8th century BC to 4th century AD) iron production sites in Upper and Lower Lusatia, Germany. *Archaeometry* 43:227–252
- Horwitz EP, Dietz ML, Fischer DE (1991a) SREX: a new process for the extraction and recovery of strontium from acidic nuclear waste streams. *Solvent Extr Ion Exch* 9:1–25
- Horwitz EP, Dietz ML, Fischer DE (1991b) Separation and preconcentration of Sr from biological, environmental and nuclear waste samples by extraction chromatography using a crown ether. *Anal Chem* 63:522–525
- Kellens N, Degryse P, Martens F, Waelkens M (2003) Iron production activities and products at Roman to early Byzantine Sagalassos. In: *Proceedings of the International Conference on Archaeometallurgy in Europe*, 24 to 26 September 2003, Milan, Italy, pp 545–554
- Ludwig KR (1980) Calculation of uncertainties of U–Pb isotope data. *Earth Planet Sci Lett* 46:212–220
- Schwab R, Höppner B, Pernicka E (2003) Studies in technology and provenance of iron artefacts from the Celtic Oppidum of Manching (Bavaria). In: *Proceedings of the International Conference on Archaeometallurgy in Europe*, 24 to 26 September 2003, Milan, Italy, pp 545–554
- Teker Y, Kusu M (2006) Fe–Mn mineralizations of Camoluk, Burdur. *Geol Bull Turk* 49(2):1–16
- Vajda N, LaRosa J, Zeisler R, Danesi P, Kis-Benedek G (1997) A novel technique for the simultaneous determination of ^{210}Pb and ^{210}Po using a crown ether. *J Environ Radioact* 37:355–372
- Wertimie TA (1980) The pyrotechnical background. In: Wertimie TA, Muhly JD (eds) *The coming of the age of iron*. Yale University Press, New Haven, pp 1–24
- White KD (1986) *Greek and Roman technology*. Thames and Hudson, London